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We report our investigations of polarization dependent recording of surface relief gratings on azobenzene containing polymer films. The experimental results indicate that the localized variations of magnitude and polarization of the resultant electric field and the existence of a nonzero component of the resultant electric field along the light intensity gradient direction in the film are essential to the formation of the surface relief gratings. Large surface modulation (>6500Å) were obtained under optimal recording conditions. It has been found that under optimal recording condition, the diffraction efficiency of the surface relief grating is dependent only on the total light energy incident on the film surface and the diffraction efficiency increase rate is proportion to the intensity of recording beams.

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Polarization Dependence of Holographic Surface Relief Gratings Recorded on Azobenzene Polymers

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Abstract

We report our investigations of polarization dependent recording of surface relief gratings on azobenzene containing polymer films. The experimental results indicate that the localized variations of magnitude and polarization of the resultant electric field and the existence of a nonzero component of the resultant electric field along the light intensity gradient direction in the film are essential to the formation of the surface relief gratings. Large surface modulation (>6500Å) were obtained under optimal recording conditions. It has been found that under optimal recording condition, the diffraction efficiency of the surface relief grating is dependent only on the total light energy incident on the film surface and the diffraction efficiency increase rate is proportion to the intensity of recording beams.

Keyword list

Surface relief gratings, Surface modulation, Azobenzene polymers, Polarization dependence, Diffraction efficiency, Trans-cis-trans photoisomerization

Introduction

Recording of refractive index and birefringence (orientation) gratings on polymers with azo dyes has been reported by several research groups during the last ten years.[1~5] The formation of the gratings was demonstrated to be strongly dependent on the polarization of recording beams. Trans-cis-trans isomerization[5~7] was suggested as the mechanism for recording the gratings in azopolymers.[1~3]

Recently, it has been reported[8~12] that surface relief gratings can be directly formed on azobenzene containing polymer films. It is certain that during the recording process, large scale molecular motion and reorientation are occurring simultaneously. However, the mechanism for the recording process is not very well understood. Since only the functionalized polymers with the azo chromophores which can participate in the trans-cis-trans photoisomerization could give rise to significant surface relief grating,[10, 13, 14] the photoisomerization certainly plays a principal role in the formation of surface relief gratings. It is well known that through the repeated trans-cis-trans photoisomerization process polarized light could induce an orientation of azobenzene groups in the direction perpendicular to the light polarization.[5~7] Polarization dependent recordings of refractive index gratings and birefringence gratings have been extensively studied and it has been established that diffraction efficiency is extremely sensitive to the polarization of the recording beams.[1~3] Very recently, we have observed that the surface relief grating formation process is also strongly dependent on the polarization of recording beams. In this paper,

we report the experimental results of the polarization and energy dependence of the grating recording process.

Experimental

An epoxy-based polymer formed by reacting diglycidyl ether of bisphenol A and 4-(4'-nitrophenylazo) phenyl amine[14,15] was used for recording the surface relief grating. The glass transition temperature of the polymer is 115° C. The polymer was dissolved in propylene glycol methyl ether acetate and 1,4-dioxane (volume ratio 3:1) with a weight ratio of 1:10. The solution was spin-coated on glass slides and baked at 70° C under vacuum for 12 hours. The typical sample thickness was about 0.8 μm.

The experimental setup for studying polarization dependence of the surface relief grating formation is shown in Fig. 1 (a). A linearly polarized laser beam at 488 nm from an Ar^+ laser is used. The polarized laser beam passes through a halfwave plate, and is then expanded and collimated. Half of the collimated beam passes through another halfwave plate and is incident on the sample directly. The other portion of the beam is reflected onto the sample from an aluminum coated mirror. Two sets of experiments were carried out. In the first set, the second halfwave plate is not in place. Laser beams with different polarizations (defined by an angle α, with respect to s-polarization) were achieved by rotating the first halfwave plate. By replacing this halfwave plate with a quarter wave plate a circularly polarized beam is obtained. In the second set, by selecting either $\alpha=0°$ or $\alpha=90°$ and positioning the second halfwave plate in one of the recording beams as mentioned earlier, two orthogonally polarized recording beams could be obtained. This recording condition is called polarization

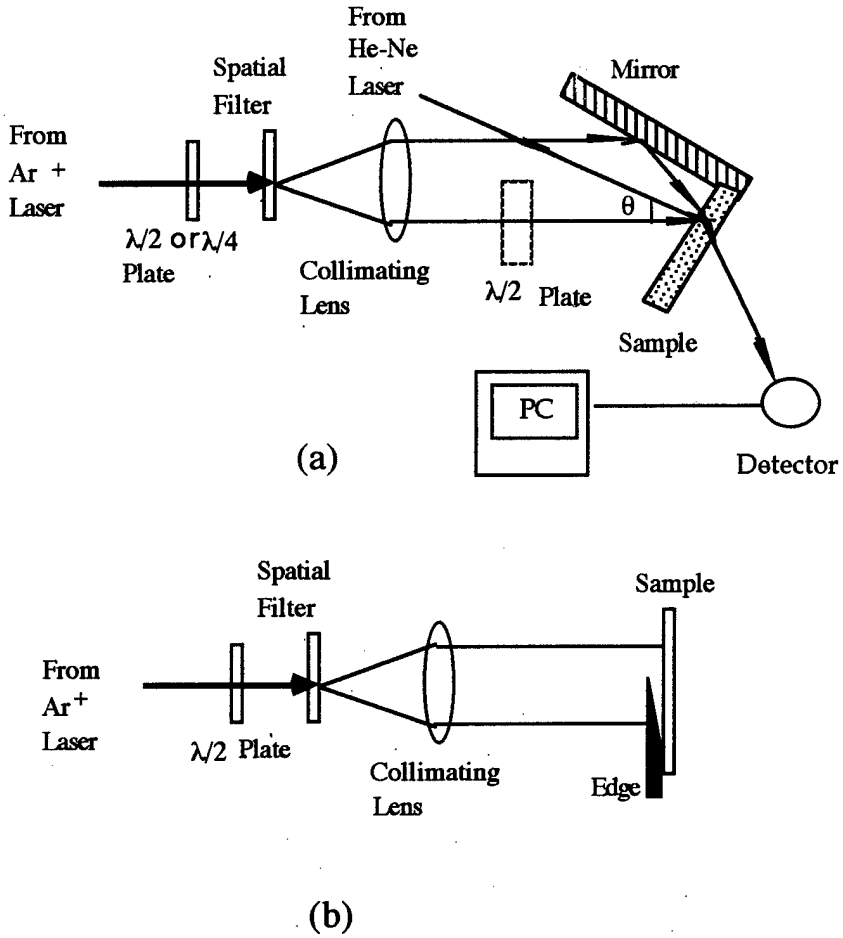

Fig. 1. Experimental setup for (a) the grating recording, and (b) the edge diffraction pattern recording using laser beams with different polarization.

recording. The typical intensity of the recording beam after the collimating lens was 55 mW/cm^2 and the recording time was about 45 minutes. The incident angle θ of the recording beams was selected to be 14°, resulting in grating spacing of about 1 μm. Due to the complex refractive index of aluminum, the beam reflected from the mirror becomes elliptically polarized except for α=0° (s-polarization) and α=90° (*p*-polarization). Therefore, in this setup, polarization states of the two recording beams usually are not identical and the power of the two beams is also slightly different. In what follows, when the recording conditions and recording intensity are mentioned, we mean the polarization state and the intensity of the beam before it is split.

To study the dependence of the formation of surface relief gratings on the recording intensity and energy, the gratings were recorded at four different intensities viz., 110, 55, 10, and 3 mW/cm^2 respectively. The recording time was chosen so that the total incident energy in the four cases was comparable and the diffraction efficiency values were not saturated. The recording condition α=45°, which will be discussed later gives the largest surface modulation, was used in this experiment.

To investigate the relation between the light intensity distribution and the surface deformation pattern, a straight edge diffraction experiment was performed as shown in the Fig. 1 (b). The space between the edge and the film is about 100μm. The film was irradiated by the laser beam with two different polarization, parallel and perpendicular to the edge. The intensity of laser beam is about 110mW/cm^2.

Results and discussions

The diffraction efficiencies and surface modulations of the surface relief gratings recorded under different polarization of recording beam are summarized in Table I. All diffraction efficiency values in the table were measured at least one day after the gratings were recorded to ensure that there are no transient effects involved.

The superposition of two recording beams with different polarizations will produce a resultant electric field with certain distribution in the film. The resultant electric field vector usually varies spatially and periodically in both magnitude and direction. It should be noted that since one recording beam is reflected from an aluminum coated mirror, the reflectivity of electric field is a complex number and it could make the distribution of the resultant electric filed even more complicated.

Under the condition for intensity recording (α=0°), interference of the two recording beams with parallel polarization will give rise to the largest light intensity variation. However, the resultant electric field is always linearly polarized and in the direction parallel to the grating grooves over the entire irradiated area (i.e., there is no spatial alternation of direction of the resultant electric field and no component of resultant electric field along the intensity gradient). Very low diffraction efficiency and small surface modulation (<100 Å) were obtained from the grating recorded. The diffraction efficiency as a function of time during the recording process is shown in Fig. 2. The rapid increase of the diffraction

efficiency at the initial stage is due to the formation of refractive index grating created by photoinduced orientation. The efficiency then dropped to a very small value and remained at that value throughout the rest of the recording process. This drop could be attributed to the cancellation of the refractive index grating by the small surface modulation.

Table I. The diffraction efficiency and surface modulation under different recording conditions

Recording conditions	Diffraction efficiency (%)	Surface modulation (Å)
$\alpha=0^\circ$	<0.01	<100
$\alpha=8^\circ$	0.4	250
$\alpha=16^\circ$	5.5	1470
$\alpha=24^\circ$	15	2140
$\alpha=45^\circ$	27	3600
$\alpha=65^\circ$	17	2770
$\alpha=90^\circ$	15.2	2540
Circularly polarized	30	3500
Polarization recording	<0.05	<100

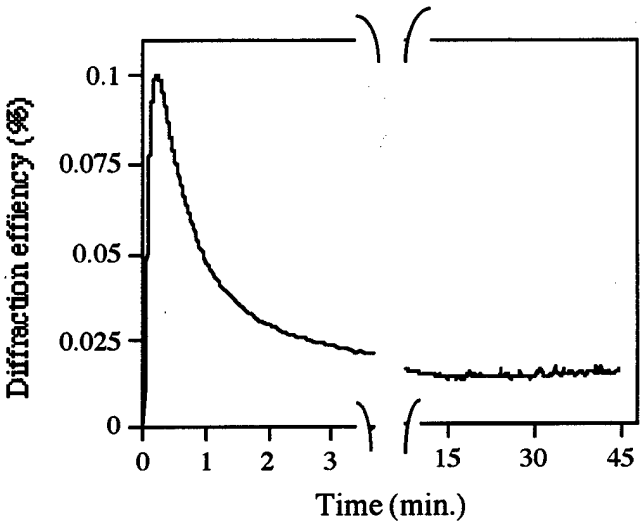

Fig. 2. Diffraction efficiency as a function of time under intensity recording.

Under the polarization recording condition, resulting from the superposition of the two recording beams with orthogonal polarization, the greatest alternation of the resultant electric field polarization occurs on the film surface. However, the light intensity on the film is uniform over the entire irradiated area. Very small surface modulation and diffraction efficiency were also obtained under this recording condition. Fig. 3 shows the diffraction efficiency as a function of time during the recording process. As the orientation grating formed, the diffraction efficiency increased, saturated and remained at a constant value throughout the rest of the recording process. After the laser beams were switched off, the diffraction efficiency decayed nearly to zero, indicating that most of the orientation grating had disappeared.

Under the other recording conditions, variations of both light intensity and the resultant electric field polarization on the film exist simultaneously. Surface relief gratings could be formed, leading to much greater values of surface modulation and diffraction efficiency than those from intensity recording and from polarization recording alone. This seems to indicate that the existence of both light intensity and

resultant electric field polarization variations is essential to the formation of surface relief gratings. It is expected that by choosing certain polarization of the recording beams, we can obtain the optimal recording conditions, under which the greatest recording rate (the derivative of diffraction efficiency with respect to time) would be achieved. Under the recording condition of α=45°, a large diffraction efficiency of 27% and the maximum surface modulation of 3600 Å were obtained for a set of polymer thin films sample. A typical grating formation process as probed by the diffraction efficiency is shown in Fig. 4. The photoinduced orientation effects leading to refractive index and orientation gratings contributed to the initial increase of the diffraction efficiency. The following stage might involve the saturation of orientation grating and partial cancellation of the refractive index grating by the surface modulation. In the later stage, the diffraction efficiency increased almost linearly until saturation. The increase of diffraction efficiency after the first minute or so of recording indicates the formation process of the surface relief grating. The gratings recorded with circularly polarized laser beams also revealed large surface modulations with high diffraction efficiencies.

During recording process, the surface modulation of a grating will increase with the incident energy of recording beam until saturated. The maximum surface modulation

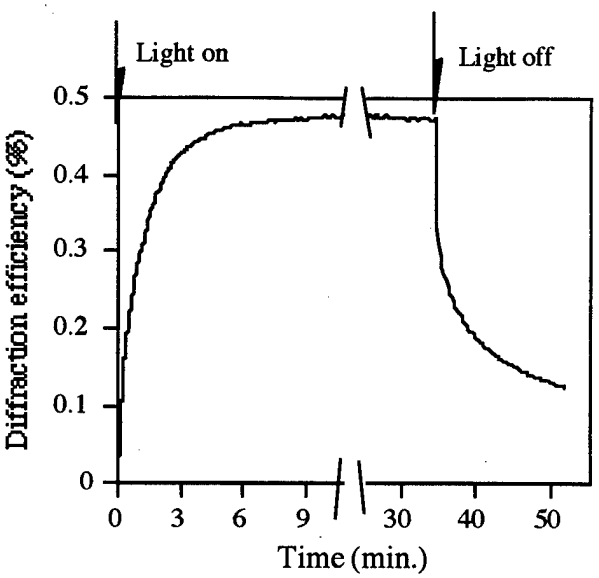

Fig.3. Diffraction efficiency as a function of time under the polarization recording condition.

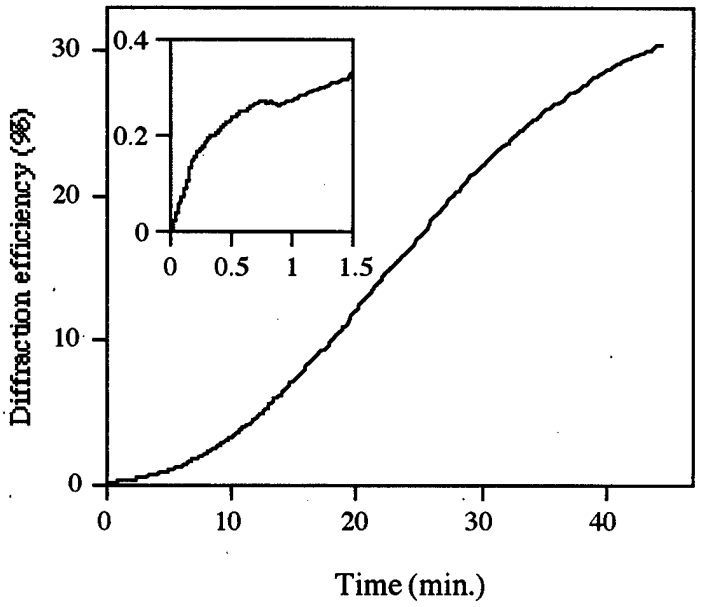

Fig. 4. Diffraction efficiency as a function of time under a mixed recording condition (α=45°). The inset shows the initial stages of the grating formation (about 90 seconds)

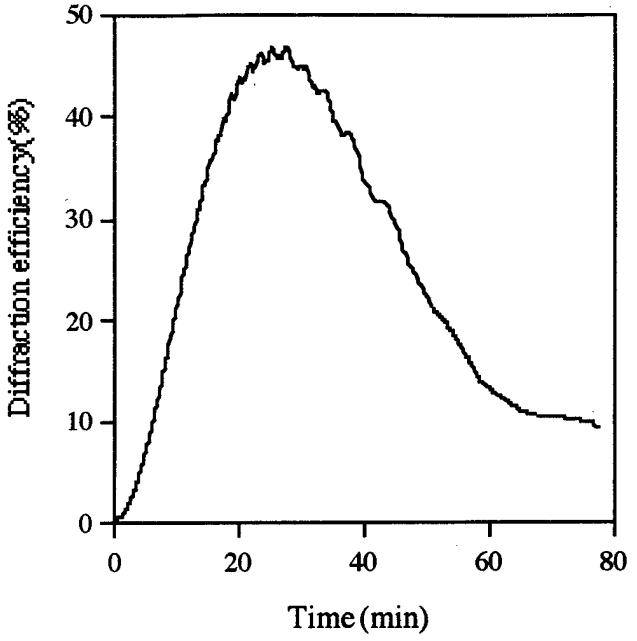

Fig. 5. Diffraction efficiency as a function of time for a grating with spacing of 1.5 μm.

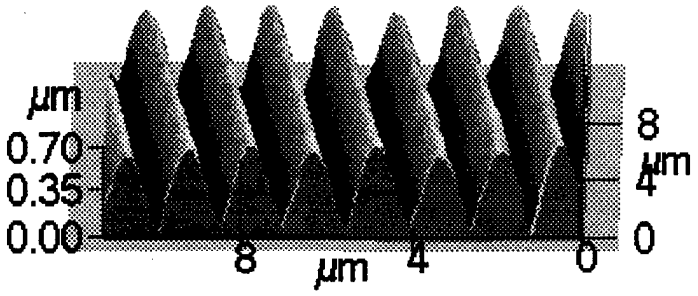

Fig. 6. AFM three dimensional view of the surface relief grating.

recorded on the polymer film is dependent on many factors such as material characteristics, recording conditions, grating spacing and the thickness of the film. The experiments investigating the influence of these factors on the maximum surface modulation are in progress. In Fig. 5, we present some experimental results to show the entire recording process of a grating with 1.5μm spacing. The grating was recorded with α=45° and incident power of 110mW/cm^2. Fig 6 is the AFM picture of the grating with spacing of 1.5 μm. The surface modulations of the grating are about 6500 Å

In the optimal recording condition (circular polarization and α=45°), the superposition of two recording beams would create a resultant electric field. which in temporal average has a non zero component in any direction. Thus, azobenzene groups would undergo many trans-cis-trans cycling without preserving any orientation. Under this situation the average number of trans-cis-trans cycles of an azobenzene group experienced will be proportional to the total energy incident on film and the rate of the photoisomerization (the number of the cycles per unit time) will be proportional to the irradiation intensity. Fig. 7 displays the diffraction efficiencies as function of energy with different intensities of the recording beam. Within the intensity range, the diffraction efficiency of the gratings is dependent only on the energy. This suggest that the recording rate of the grating is proportional to the intensity and thus, to the rate of the photoisomerization. In the photoisomerization process, an azobenzene group would undergo repeated trans-cis-trans cycling until its orientation is perpendicular to the polarization of light. To study the alignment of azobenzene group by a linearly polarized light, we have carried out a simple experiment, in which a polymer thin film (<0.4μm) was exposed to a polarized laser light at 488 nm with an intensity of about 70mW/cm^2 and the absorption change of the film was monitored by a lower intensity laser beam from another laser with the same light polarization and wavelength. The experimental results show that the

absorption drops to about 70% of initial value within the first 60 second and keeps this value during the rest of irradiation. These results suggest that during the irradiation the azobenzene can be aligned by polarized light but the alignment would be thermally re-randomized. Therefore, the difference of photoisomerization rate before and after the absorption saturated is not significantly large. In somerecording condition such as $\alpha=90^{\circ}$, the photoisomerization could buildup a spatially varied distribution of the azobenzene group alignment. This can lead to a decrease of the photoisomerization rate. In the optimal condition, as discussed above, the photoisomerization process can not induce a temporary stable distribution of azobenzene group alignment. The photoisomerization caused under this condition would be much larger than that under the exposure condition of $\alpha=90^{\circ}$. It might be the reason that with the same irradiation energy, the surface modulations formed under the optimal polarization condition are much larger than under condition $\alpha=90^{\circ}$.

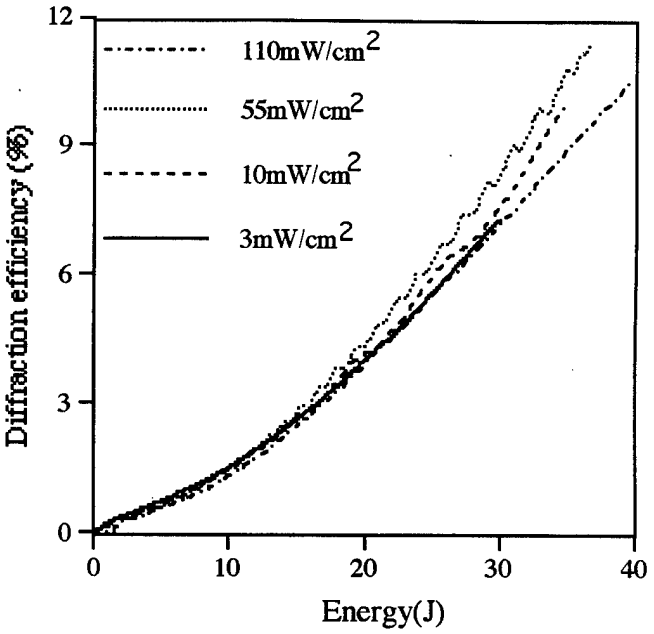

Fig. 7. Diffraction efficiency of the surface grating as functions of recording power and energy.

Similar to the result of grating recording with s-polarized beam, in the edge diffraction pattern recording experiments when the polarization of the irradiation beam is parallel to the edge, no regular pattern of surface deformation was formed on the film surface. When the polarization of the laser beam is perpendicular to the edge, a regular surface relief pattern was recorded as shown in Fig. 8. The intensity distribution on the surface of the film produced by the edge diffraction can be evaluated by the near filed diffraction theory. Fig. 9 displays the light intensity distribution and the negative of the first order derivative of the light intensity. Comparing the modulation profile in Fig. 8 and negative of the derivative of the light intensity in Fig. 9, one can clearly see that the surface profile maps the negative of the derivative of the light intensity. This can be expressed as:

$$S(x) = -\gamma \frac{dI(x)}{dx} \qquad (1)$$

here S(x) is the surface profile, I(x) is the light intensity and γ is a constant.

By analyzing the results of recording of surface relief grating and edge diffraction pattern, we have found that there must exist light intensity variation in order to produce surface modulation. The grating grooves should be perpendicular to the light intensity gradient on the surface. The distinct differences of the resultant electric field distribution formed by the condition of $\alpha=0^{\circ}$ and others in the grating recording,

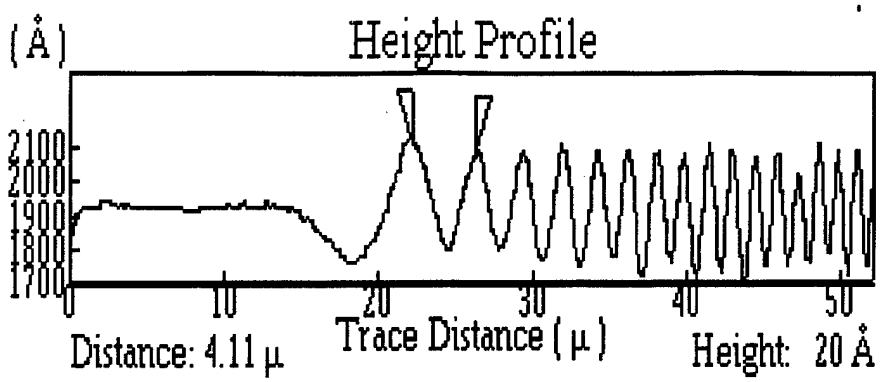

Fig. 8. AFM height profile of recorded edge diffraction pattern.

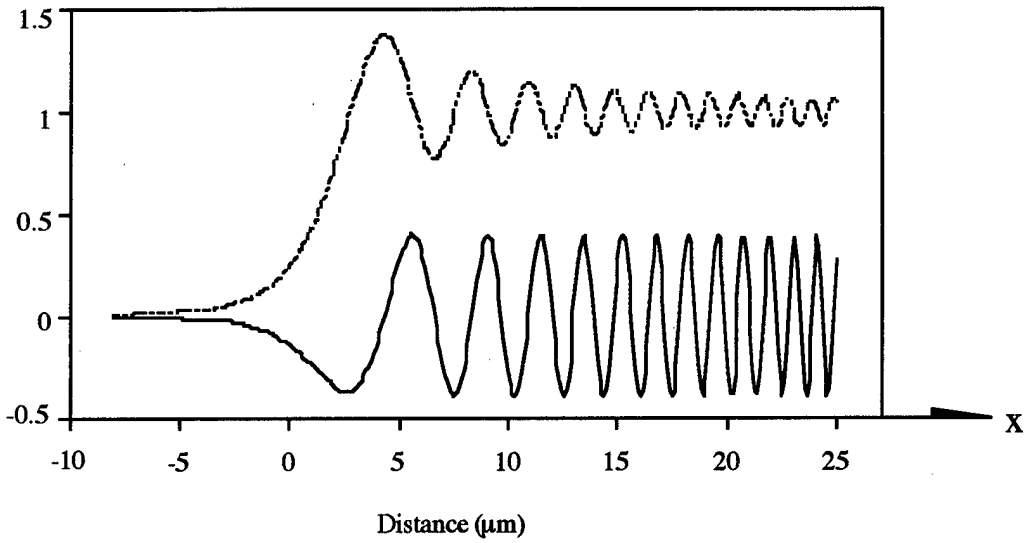

Fig. 9. Intensity distribution produced the edge diffraction (dotted line) and the negative of the first order derivative of the intensity distribution (solid line).

and by laser beams with polarization parallel to and perpendicular to the edge in the edge diffraction pattern recording are whether the resultant electric field has a component in the direction of the light intensity gradient. It appears that the polymer chains could move along the direction of the resultant electric field. Only when there is an intensity gradient in some direction with a nonzero component of the resultant electric field, the surface modulation pattern could be formed in this direction. Considering this relation of the intensity gradient and the resultant electric field, one can rewrite the equation (1) as:

$$S(x) = -\gamma \vec{E} \bullet \vec{\nabla} \left| \vec{E} \right| \qquad (2)$$

Here E is the resultant electric filed. The constant γ should be dependent on the photoisomerization rate as we discussed above.

Conclusion

We have observed that the formation of surface relief gratings on the azobenzene containing polymer films strongly depends on the polarization of the recording beams. Very large surface modulation could be achieved under the optimal recording conditions. After analyzing the resultant electric field vector distribution produced by interference of two recording beams and the edge diffraction, we believe that the existence of spatial variations of both magnitude and direction of the resultant electric field vector and nonzero component of resultant electric field along the gradient of light intensity in the films are essential conditions to induce surface modulations. The results of polarization dependent experiments imply that spatially varying thermal effects due to light absorption is not sufficient to record the large surface relief gratings. The trans-cis-trans photoisomerization certainly play the most important part in the formation of the surface relief grating. The experimental results clearly show that under optimal recording condition, the recording rate is proportion to the rate of photoisomerization and the diffraction efficiency values of surface relief gratings are only dependent on total irradiation energy.

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